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THE IMPORTANCE OF EXCHANGE REACTIONS IN CONTROLLED/LIVING
RADICAL POLYMERIZATION IN THE PRESENCE OF
ALKOXYAMINES AND TRANSITION METALS

by

K. Matyjaszewski

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Carnegie Mellon University
Department of Chemistry
4400 Fifth Avenue
Pittsburgh, PA 15213

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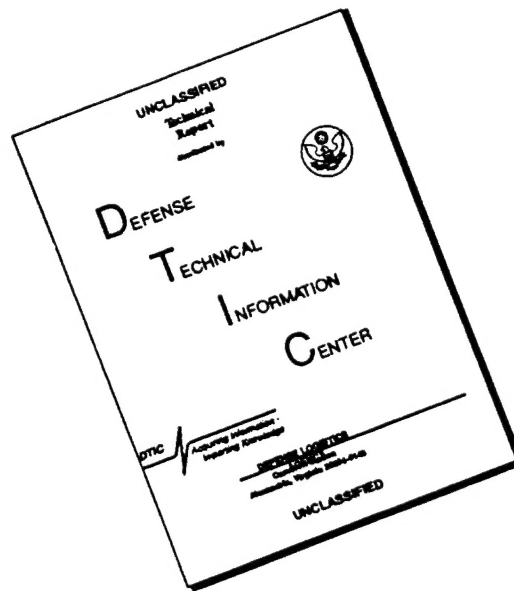
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THE IMPORTANCE OF EXCHANGE REACTIONS IN CONTROLLED/LIVING RADICAL POLYMERIZATION IN THE PRESENCE OF ALKOXYAMINES AND TRANSITION METALS

Krzysztof Matyjaszewski

Department of Chemistry, Carnegie Mellon University,
4400 Fifth Avenue, Pittsburgh PA, 15213

Abstract: The role of exchange reactions in controlled/living radical polymerizations is analyzed. Styrene polymerization in the presence TEMPO and atom transfer radical polymerization (ATRP) catalyzed by transition metals ($\text{Cu}^{\text{II}}\text{X}_2/2\text{Bipy}$ complex) are compared. ATRP proceeds approximately one order of magnitude faster than TEMPO-moderated polymerization due to a higher stationary concentration of radicals and an equilibrium more shifted to the side of radicals. ATRP can provide better defined polymers with polydispersities down to $M_w/M_n \approx 1.05$. This fact can be ascribed to a faster deactivation process and a smaller contribution of side reactions. The polydispersities in both systems are defined by the relative rates of the deactivation and propagation processes. The rate constant of deactivation of growing polystyryl radicals by TEMPO is in the range of $k_d \approx 10^8 \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$, which is substantially higher than the previously reported value.

INTRODUCTION

Radical polymerization is entering a renaissance stage. This resurgence can be ascribed to new methods for reliable measurements of rate constants of the elementary reactions involved in the process and also to new methods for the synthesis of well-defined polymers. For example, atom transfer radical polymerization (ATRP) allows the preparation of various (co)polymers with polymerization degrees defined by the ratio of concentrations of reacted monomer to the introduced initiator, $\text{DP}_n = \Delta[\text{M}]/[\text{I}]_0$, low polydispersities, $1.04 < M_w/M_n < 1.5$, within a large range of

molecular weights, $300 < M_n < 100,000$ [1-3]. ATRP can be used for the polymerization of styrenes, dienes, acrylates, methacrylates, acrylonitrile, and other monomers [4-7]. It also allows facile preparation of (co)polymers with novel controlled chain architectures, chain composition and functionalities, as shown in Fig. 1.

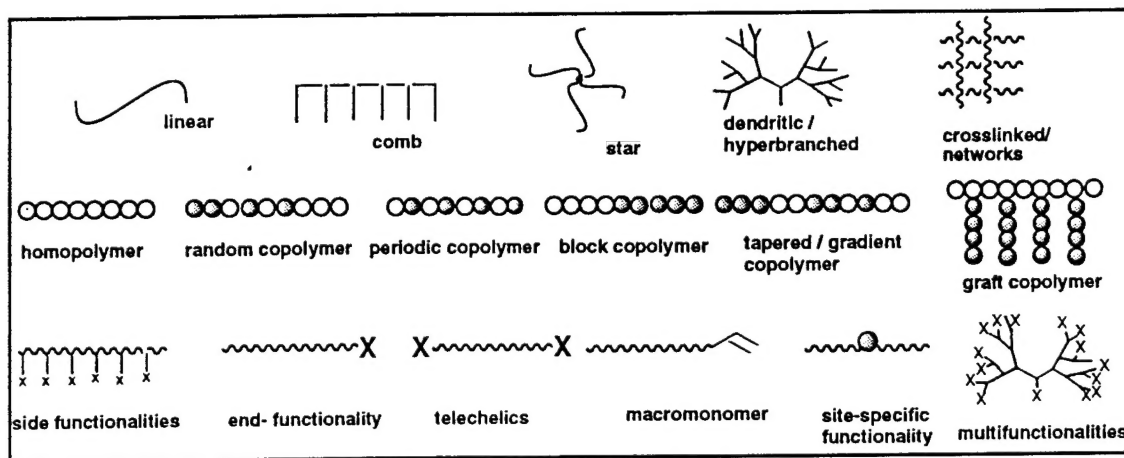


Fig. 1. Examples of controlled chain topologies, composition and functionalities which can be obtained by ATRP of styrenes, (meth)acrylates, acrylonitrile and other vinyl monomers

The recent progress in radical polymerization originates in the rational use of dynamic equilibria between growing radicals and dormant species [8]. ATRP and various other systems which use either stable radicals such as TEMPO [9-12], organometallic derivatives [13-15] or degenerative transfer [16] share this common characteristics. In all of these systems control of molecular weights and reduced polydispersities can be ascribed to the exchange between growing radicals and various forms of dormant species. This paper will discuss the importance of exchange processes and the fundamentals of controlled/living radical polymerizations.

RESULTS AND DISCUSSION

Fundamentals of Controlled/Living Polymerization

In the purist sense, a living polymerization is a chain growth process without irreversible chain transfer and chain termination [17, 18]. In many real systems, chain breaking reactions do occur, and depending on their contribution, it is possible to rank such "living" systems [19]. Chain breaking reactions lead to a loss of functionality of growing chains and their contribution (i.e. proportion of dead chains) increases with conversion and with the chain length. Figs. 2 a and b illustrate the proportion of chains which are active and overall polydispersities as a function of conversion (and chain length) for systems with fast initiation and various chain breaking reactions using $[M]_0 = 10$ mol/L and $[I]_0 = 0.1, 0.01$ and 0.001 mol/L. The coefficients of (pseudo)unimolecular termination, k_t/k_p , (pseudo)unimolecular transfer, k_{tr}/k_p , and transfer to

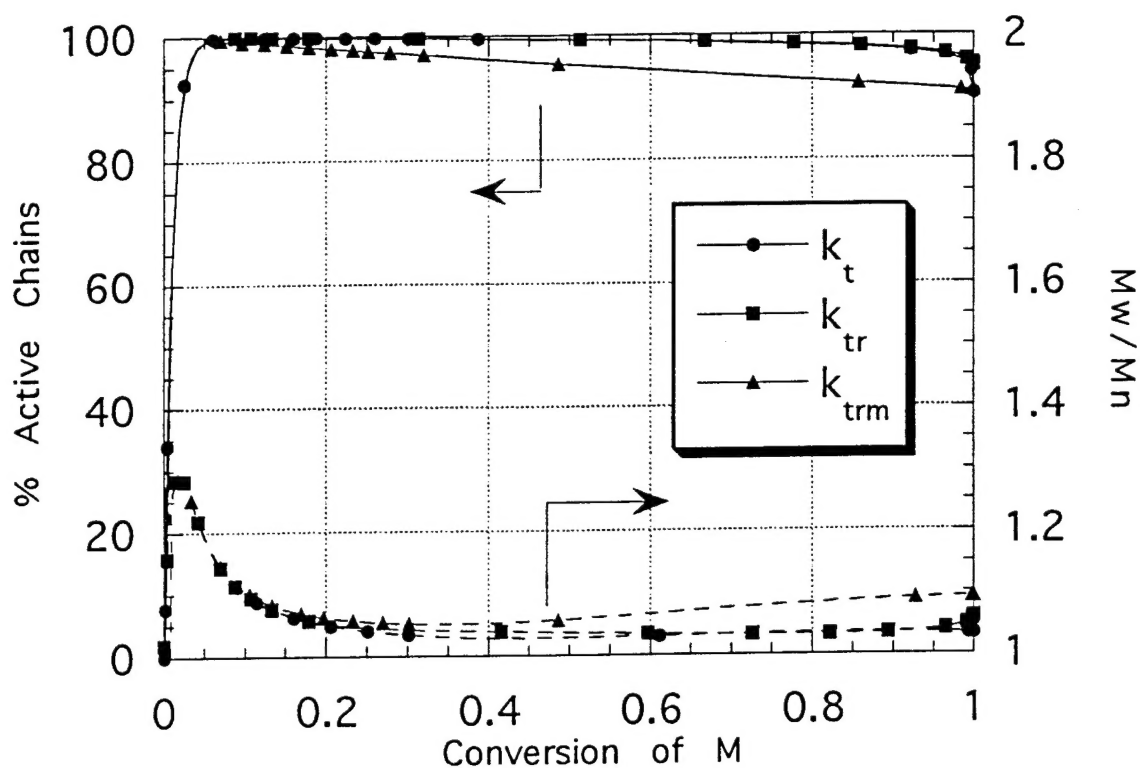


Fig. 2a. Proportion of active chains and polydispersities as a function of monomer conversion for the ratios of $k_x/k_p=0.001$ and $[M]_0=10$ mol/L and $[I]_0=0.1$ mol/L.

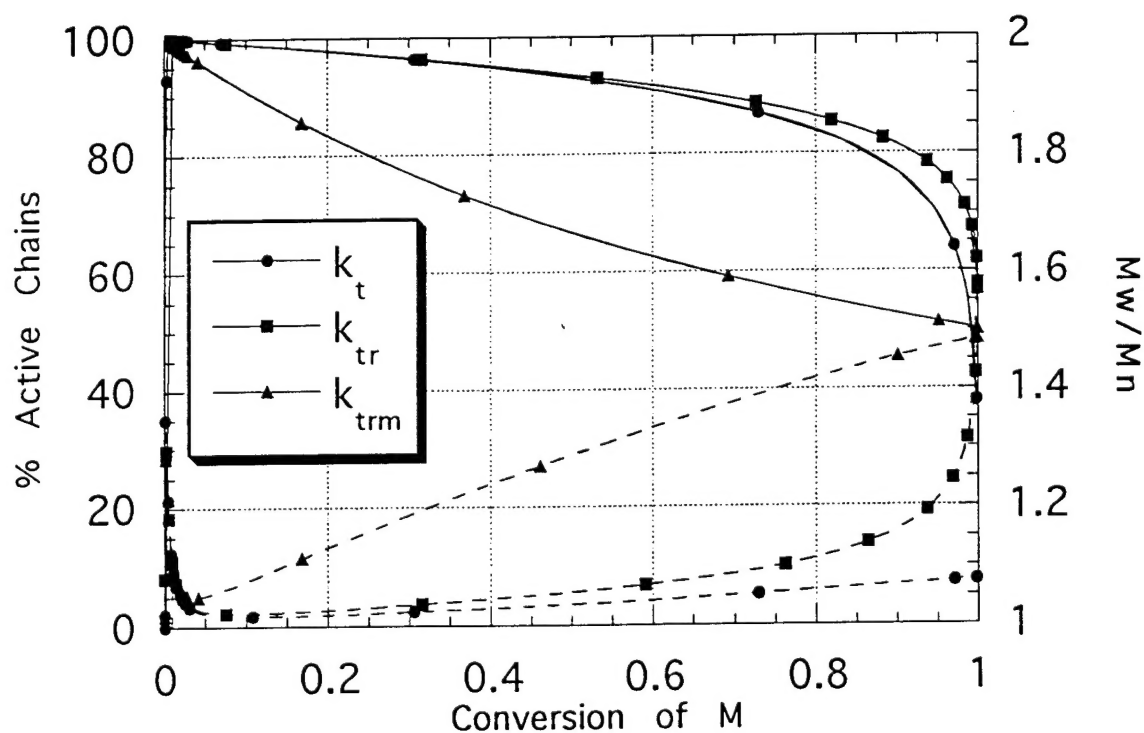


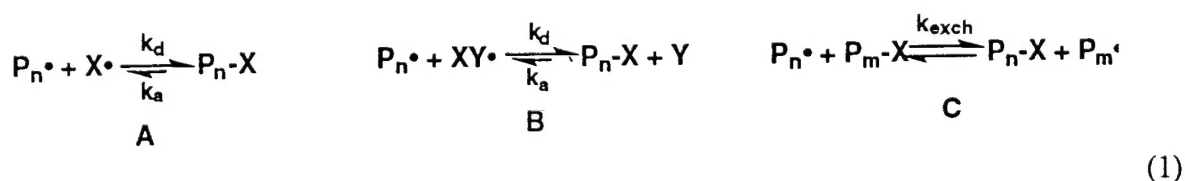
Fig. 2b. Proportion of active chains and polydispersities as a function of monomer conversion for the ratios of $k_x/k_p=0.001$ and $[M]_0=10$ mol/L and $[I]_0=0.01$ mol/L.

monomer, $k_{tr}M/k_p$, were arbitrarily chosen as 10^{-3} . As can be seen clearly from Fig. 2a, nearly perfect polymers can be prepared with $DP \approx 100$, however, significant deviations and difficulties are observed for the synthesis of polymers with $DP \approx 1000$ (Fig. 2b), whereas the synthesis of well-defined polymers with $DP \approx 10,000$ fail.

Especially instructive (and surprising) is the case shown for k_t in Fig. 2b. Although the polydispersities stay very low till the very end of the reaction ($M_w/M_n < 1.1$), 20% of the chains are irreversibly deactivated at 90% monomer conversion, and half of the chains have lost their activity at 99% conversion. This is a very important information for polymer chain end functionalization and block copolymer synthesis. Nevertheless, it is still possible to prepare polymers with controlled molecular weights, low polydispersities and a high degree of chain end functionality in the presence of transfer and termination, if the chains are sufficiently short (Fig. 2a).

Indeed, the main application of controlled/living polymerizations is the preparation of well defined (co)polymers with predetermined molecular weights, low polydispersities, controlled end-functionalities and the synthesis of block copolymers. However, the absence or low contribution of irreversible chain breaking reactions is not a sufficient prerequisite for such syntheses. It is also necessary that all chains have the same chance of growth, meaning that they should be initiated at the same time and exchange rapidly if they have different reactivities. Slow initiation and slow exchange have opposite effects on polymerization than chain breaking reactions. In this case, control of the polymerization increases (!) with increasing chain length and conversion. This behavior is observed because more exchange reactions and more complete initiation will occur for longer chains. Initiation efficiency has been already quantitatively analyzed before but the importance of exchange reactions has been realized only recently, especially for ionic reactions [20-22].

There are several possible radical exchange systems:



Case A refers to systems that employ TEMPO, other nitroxides, cobaltoximes and other stable radicals that form covalent species capable of spontaneous homolytic cleavage. It is also possible that a radical can be reversibly deactivated by a species possessing an even number of electrons which would lead to a persistent radical as a dormant species [23]. System B describes a catalyzed process in which a catalyst Y participates in the homolytic cleavage of dormant species, like in ATRP. The last case, C, illustrates a degenerative transfer process in which the active species,

P_n^\bullet , reacts reversibly with the dormant species, P_m-X , via a bimolecular transfer of the protective group, X. In both cases, B and C, the dormant species do not cleave spontaneously.

In each of these systems, the polydispersities and molecular weight control are defined by the relative ratios of the rates of deactivation (occurring with the rate constant of deactivation, k_d) and propagation (k_p). At complete conversions, the polydispersities of many systems with slow exchange are defined by a very simple equation (2) [20]:

$$M_w/M_n = 1 + ([I]_0 k_p) / ([D] k_d) \quad (2)$$

where $[D]$ is the concentration of deactivating agent (X or YX) that deactivates growing chains with a rate constant, k_d . If deactivation is unimolecular (ion pair, caged radicals), then $[D]$ is omitted in eq. 2. Equation 2 is valid for systems in which the equilibrium is strongly shifted to the side of the dormant species, sufficiently long chains are formed and the polydispersities do not significantly exceed 2. $[I]_0$ is the total concentration of initiator (or chains) and k_p is the absolute rate constant of propagation for the growing species. For the degenerative transfer process (case C) concentrations of deactivator and t chains are nearly identical and therefore eq. 2 simplifies to the equation 3:

$$M_w/M_n = 1 + k_p / k_{exch} \quad (3)$$

The evolution of polydispersities with conversion for three systems with the ratios of $([I]_0 k_p) / ([D] k_d) = 0.01, 0.1$ and 1 is shown in Fig. 3. If the ratio is smaller than 1, then the rate of activation does not affect the polydispersities. However, for ratios ≥ 1 , a small effect of the rate of activation can be noticed. The overall polydispersities were calculated without taking into account the residual initiator and therefore are smaller than those with the initiator taken into account [18].

Figure 3 shows that the polydispersities decrease with conversion and are lower for both lower initiator concentrations (longer chains) and faster deactivation (higher $[D]$, higher k_d/k_p). Thus, polymers with lower polydispersities can be prepared for the chains with the same length, providing that the deactivation process is faster. This rate increase can be accomplished by using either a higher concentration of deactivator or a more reactive deactivator (higher k_d). The effect of slow exchange discussed above is valid for systems when slow exchange is the only reason for elevated polydispersities. If an additional side reaction (transfer, termination, etc.) participates then the polydispersity should increase with conversion, leading to a certain "window" of polymerization degrees at which well defined polymers can be prepared. This case is probably the most realistic one. At a low range of molecular weights the polydispersities are higher than in ideal

systems due to slow exchange but they increase at a high range due to progressively more important side reactions.

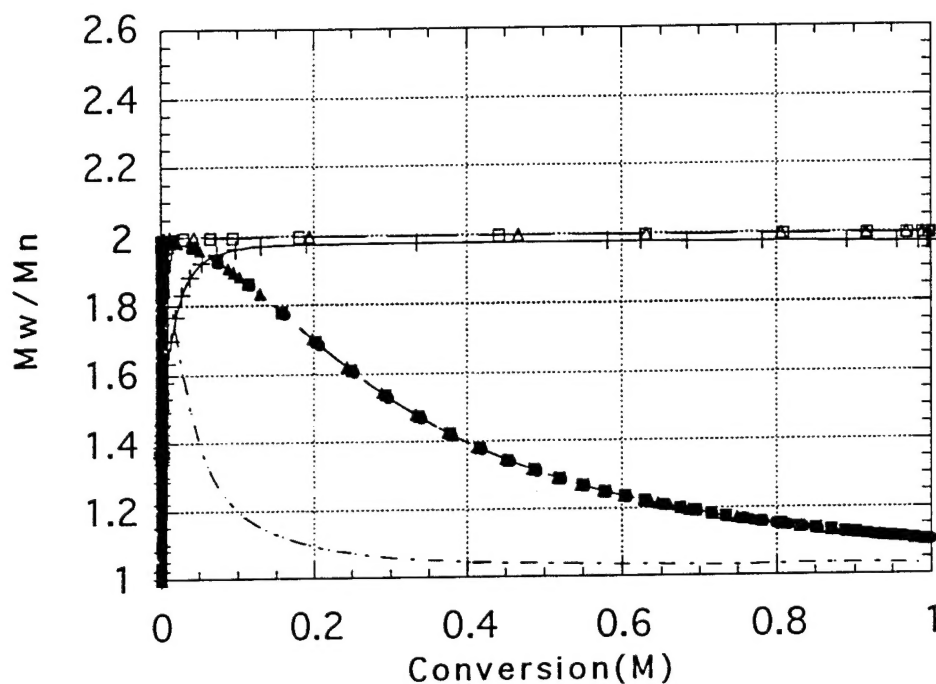


Fig. 3. Dependence of polydispersities on conversion for systems with slow exchange and with the ratio of $([I]_0 k_p)/([D] k_d) = 0.01$ (---), 0.1 (variable k_a : ■, ▲, ●) and 1 (variable k_a : +, △, □).

Comparison of Styrene Polymerization by ATRP and in the Presence of TEMPO

1. Kinetics, Molecular Weights and Polydispersities

Figure 4 presents typical kinetic plots for the radical polymerization of styrene in the presence of variable concentrations of a TEMPO adduct (2,2,6,6-tetramethyl-1-(1-phenylethoxy piperidine)) at 120 °C and for ATRP initiated by 1-phenylethyl bromide in the presence of 0.1 mol/L CuBr/2Bipy at 110 °C.

This plot shows that the polymerization rate does not depend on the concentration of the TEMPO derivative and is very close to the thermal polymerization rate. These results indicate that the main reason for the similar rates despite the presence of variable concentrations of alkoxyamines is that the thermal self-initiation of styrene is responsible for maintaining a reasonable polymerization rate. The contribution of thermal self-initiation is so significant due to the extremely low value of the equilibrium constant. The main role of the alkoxyamines is to control molecular weights and polydispersities by exchanging with thermally generated radicals. This exchange may be uni- or bimolecular. This partially explains why the TEMPO-moderated

polymerization of (meth)acrylates, which do not self-initiate, is much less successful than that of styrene [24]. At the same time ATRP is much faster and it is first order in respect to the dormant alkyl bromide [3].

The estimated equilibrium constant for styrene polymerization in the presence of TEMPO is $K \approx 10^{-11}$ mol/L at 120 °C whereas that for ATRP is $K \approx 10^{-8}$ at 110 °C. These values were obtained from computer simulations of the kinetics, molecular weights and polydispersities but they also can be simply estimated from the stationary concentration of radicals (P^\bullet), dormant species ($P-X$), scavenger (X^\bullet), and activator.

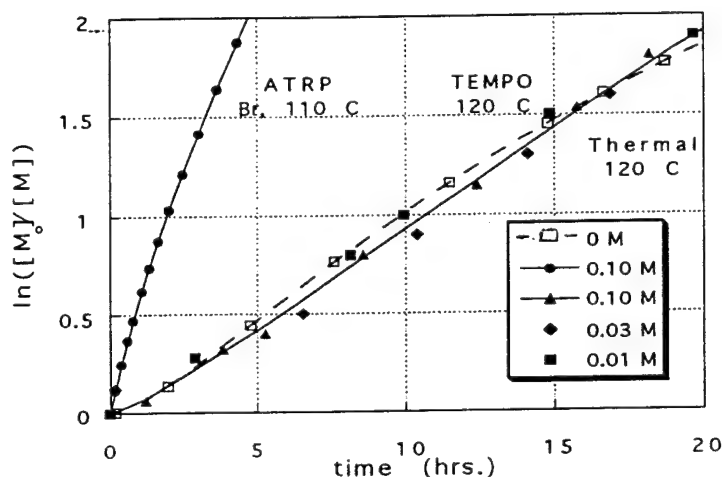


Fig. 4. Kinetics of styrene bulk polymerization by ATRP at 110 °C (\bullet $[1\text{-PhEtBr}]_0 = 0.1$ mol/L, $[\text{CuBr}]_0 = 0.1$ mol/L, $[\text{dNBPY}]_0 = 0.2$ mol/L); thermal process at 120 °C (\square) and in the presence of 1-phenylethyl TEMPO at 120 °C (\blacktriangle 0.1 mol/L, \blacksquare 0.03 mol/L, \blacklozenge 0.01 mol/L)

The value of $[P^\bullet]_{st}$ can be calculated from the observed rate coefficients (slopes of the kinetic plots in Fig. 4, $k_{obs} = d\ln[M]/dt$) and the known propagation rate constant, k_p^\bullet [25]:

$$[P^\bullet]_{st} \approx k_{obs}/k_p^\bullet \quad (4)$$

$[P^\bullet]_{st}$ equals $\approx 10^{-7}$ mol/L at ≈ 110 °C for the ATRP and $\approx 10^{-8}$ mol/L at ≈ 120 °C for the TEMPO systems. Recent EPR estimates of the stationary concentration of TEMPO indicate that approximately 0.1% to 0.3% of TEMPO is present with respect to the starting adduct or initially used TEMPO [26, 27]. Thus, the value of the equilibrium constant for the TEMPO-mediated polymerization is:

$$K_T = ([P\bullet]_{st} [TEMPO]_{st}) / [P-TEMPO] \approx 10^{-8} \text{ mol/L} \times 10^{-3} \approx 10^{-11} \text{ mol/L} \quad (5)$$

On the other hand, in ATRP there is approximately 1 to 10% of the stationary Cu^{II} with respect to Cu^I [3]. Taking the lower value (1%), the equilibrium constant for ATRP equals:

$$K_A = ([P\bullet]_{st} [X-Cu^{II}]) / ([P-X] [Cu^I]) \approx 10^{-7} \text{ mol/L} \times 10^{-2} / 10^{-1} \text{ mol/L} \approx 10^{-8} \quad (6)$$

For a better comparison, the latter K_A value can be multiplied by the concentration of the activator (Cu^I), to yield $K = 10^{-9} \text{ mol/L}$, roughly two orders of magnitude higher than K_T . This result explains why ATRP is a much faster process.

Figures 5 and 6 illustrate the evolutions of polymerization degrees and polydispersities with conversion for three systems. The data were simulated using the equilibrium constants discussed above and assuming that growing radicals are trapped by the corresponding scavengers with the rate constants of deactivation $k_d \approx 10^8 \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$. ATRP displays a linear dependence of molecular weights on conversion that is very close to the theoretical line and displays the lowest polydispersities. The TEMPO system provides also satisfactory agreement with theoretical values of DP. The polydispersities also decrease with conversion but they are slightly higher than in the case of ATRP. Thermal polymerization provides very high molecular weight polymers with M_n values in the range 300,000 to 400,000 and polydispersities in the range $M_w/M_n \approx 2$.

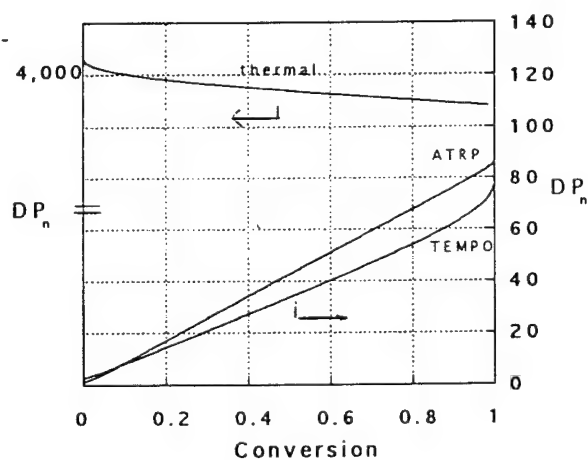


Fig. 5. Dependence of polymerization degrees on conversion for styrene bulk polymerization by ATRP at 110 °C (● $[1-PhEtBr]_0 = 0.1 \text{ mol/L}$, $[CuBr]_0 = 0.1 \text{ mol/L}$, $[dNBPY]_0 = 0.2 \text{ mol/L}$); thermal process at 120 °C (□) and in the presence of 1-phenylethyl TEMPO at 120 °C (◆ 0.1 mol/L).

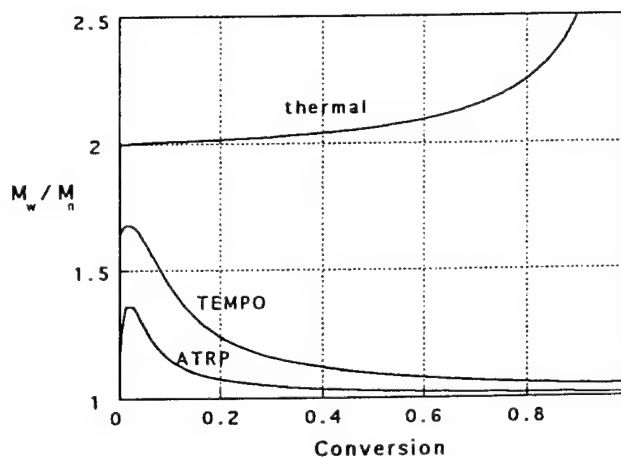
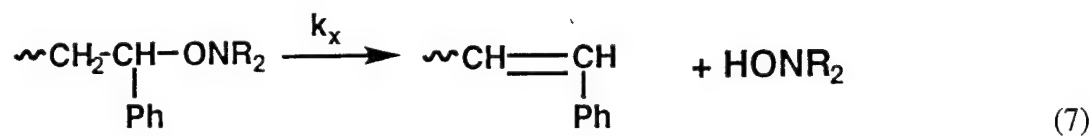


Fig. 6. Evolution of polydispersities with conversion for styrene bulk polymerization by ATRP at 110 °C (● [1-PhEtBr]₀ = 0.1 mol/L, [CuBr]₀ = 0.1 mol/L, [dNBPY]₀ = 0.2 mol/L); thermal process at 120 °C (□) and in the presence of 1-phenylethyl TEMPO at 120 °C (◆ 0.1 mol/L).

The experimental values of polydispersities are higher than those predicted by the ideal behavior in which, in addition to propagation and termination, only exchange reactions operate. The higher polydispersities must be due to the contribution of some additional side reactions. It was found that thermal self-initiation, although very important for maintaining reasonable polymerization rates in the presence of TEMPO results only in a minor enhancement of polydispersities. The same is true for transfer to monomer under such conditions. It is proposed that the decomposition of alkoxyamines, observed earlier for model species [28], is at least partially responsible for higher polydispersities:



The rate constant $k_x = 10^{-5} \text{ s}^{-1}$ calculated for oligomeric/polymeric species is lower than that measured for the 1-phenylethyl derivative [28] due to the statistical 2/3 availability of β-H atoms. The decomposition can occur as an unimolecular process, however, it is also reasonable that TEMPO, approaching growing radical, may react not only with the C-centered radical but may also abstract a β-H atom.

Other side products have been detected in the direct reaction of TEMPO with styrene during self-initiation [29]. These products include 1,2- diadducts of TEMPO with styrene and coupling products of the Mayo dimer with TEMPO. Apparently, these products can also form growing chains because there is a relatively good agreement between measured and predicted molecular weights in systems initiated by adducts, by BPO and AIBN in the presence of TEMPO and initiated thermally in the presence of TEMPO as well [11, 30, 31].

2. Concentration of Various Species.

It is perhaps the most instructive to analyze and compare the concentrations of various species in ATRP with those in TEMPO-mediated polymerization. After a short initial non-stationary period, the concentration of dormant chains in both systems stays rather constant up to relatively high conversions. Because ATRP is faster, the proportion of chains terminated by coupling is higher than for TEMPO systems but does not exceed 5% of all chains. For the same reason, the proportion of chains due to self-initiation and to transfer with the Mayo dimer is lower for ATRP.

The initial concentration of radicals in either system depends on the amount of excess scavenger. If neither free TEMPO nor CuX_2 is initially added, then the initial radical concentrations are defined by the equilibrium constant and initiator concentrations; e.g. for $[\text{P-TEMPO}]_0 = 0.1 \text{ mol/L}$:

$$[\text{P}\cdot]_0 = (K_T [\text{P-TEMPO}])^{0.5} \approx 10^{-6} \text{ mol/L} \quad (8)$$

and for ATRP with $[\text{P-X}]_0 = 0.1 \text{ mol/L}$ and $[\text{CuX}]_0 = 0.1 \text{ mol/L}$:

$$[\text{P}\cdot]_0 = (K_A [\text{P-X}][\text{CuX}])^{0.5} \approx 10^{-5} \text{ mol/L} \quad (9)$$

For both systems the initial concentrations of both scavengers (TEMPO and CuX_2) are equal to those of the radicals. At this very high concentration, the radicals undergo rapid bimolecular termination which reduces their concentration to 10^{-8} and 10^{-7} mol/L , respectively for TEMPO and ATRP (Figure 7). The concentrations of scavengers increase simultaneously to 10^{-5} and 10^{-4} mol/L , respectively for TEMPO and CuX_2 . These values agree with the experimentally observed $\approx 0.1\%$ of TEMPO and $\approx 1\%$ of CuX_2 for both scavengers under equilibrium conditions.

Thus, both systems have a self-correction mechanism in which via a rapid initial termination process they produce an excess of scavengers which are responsible for the controlled polymerization. Such an effect has also been observed in conventional organic radical reactions and termed the persistent radical effect [32].

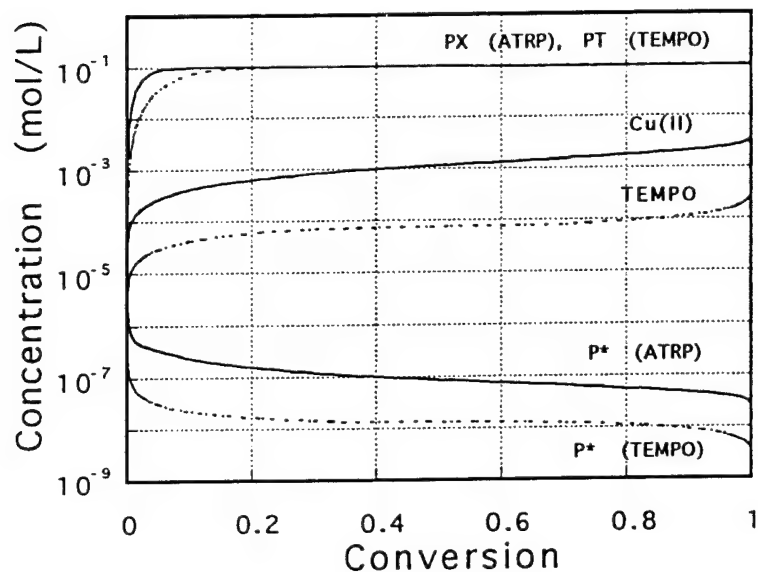


Fig. 7. Simulated dependence of the concentrations of scavengers, dormant chains and growing radicals in ATRP and TEMPO systems.

The initial fast termination may be accompanied by a loss of control of molecular weights and higher polydispersities but this situation progressively improves with conversion. It is possible to improve the systems further by addition of small amounts of scavengers at the beginning of the reaction. Under such conditions polymers with lower polydispersities can be prepared. In fact, a small amount of TEMPO is formed by slow decomposition of the adduct upon storage and Cu^{I} halides can be slowly oxidized to Cu^{II} upon storage as well. Thus, it is beneficial not to remove such "impurities" [1].

3. Dynamics of Exchange

As discussed earlier, the polydispersities decrease with conversion in systems with relatively slow exchange. The shape of such a decrease and the values of the final polydispersities can be used to estimate the relative rate of the deactivation process (cf. eq. 2). Such an evaluation is possible only when slow exchange is the only reason for the elevated polydispersities. Otherwise, it is necessary to know the precise contribution of the side reactions and use a computer simulation of the entire process. Because side reactions are less important at the very beginning of the polymerization, it is possible to deduce the relative rate of deactivation from the initial decrease

of the polydispersities with conversion. Rough estimates made for TEMPO and ATRP, indicate that the ratios $k_p/(k_d[D]_{st})$ are approximately 10^{-1} and $10^{-3} \text{ mol}^{-1}\text{L}$, respectively. The value of k_d can then be estimated by using known values of the propagation rate constant of styrene ($k_p \approx 2,000 \text{ mol}^{-1}\text{L s}^{-1}$ at 120°C [25]), and the previously discussed $[\text{TEMPO}]_{st}$ and $[\text{CuX}_2]_{st}$ values. It appears that both scavengers react very rapidly with growing radicals with the rate constant $k_d \approx 10^8 \text{ mol}^{-1}\text{L s}^{-1}$. If the stationary concentration of CuX_2 is 10% the rate constant of deactivation may be $\approx 10^7 \text{ mol}^{-1}\text{L s}^{-1}$.

There is another method to estimate a lower limit for the deactivation rate constant. The degrees of polymerization formed at low conversion (when the stationary state is already established) are defined by the ratio of the rates of propagation and deactivation:

$$\text{DP}_0 \approx R_p/R_d = (k_p[M]_0[P\cdot]) / (k_d[D]_{st}[P\cdot]) \leq 1 \quad (10)$$

Indeed, at the very beginning of the polymerization, especially when a small amount of the scavenger is added or formed due to the persistent radical effect ($\approx 1\%$ of CuX_2 and $\approx 0.1\%$ TEMPO), there is a very good control of molecular weights and a linear evolution of molecular weights with conversion (cf. Fig. 5) when the initiators are used at high concentrations ($[\text{P-X}] \approx 0.1 \text{ mol/L}$). However, when TEMPO is used at lower concentrations with the targeted molecular weight in the range of $M_n \approx 100,000$, then the oligomers with $\text{DP}_n \approx 10$ are initially formed.

Since $[\text{TEMPO}]_{st} \approx 10^{-5} \text{ mol/L}$ ($\approx 0.1\%$ from $[\text{P-TEMPO}]_0 \approx 10^{-2} \text{ mol/L}$), it is possible to estimate a value for k_d :

$$k_d \approx (k_p[M]_0) / (\text{DP}_0 [D]_{st}) \approx 10^8 \text{ mol}^{-1}\text{L s}^{-1} \quad (11)$$

which is in a good agreement with the previously discussed values and also with the known rates of the reaction of TEMPO with model 1-phenylethyl radical [33].

It has been proposed recently that the rates of deactivation of polymeric radicals with TEMPO are much smaller and in the range of $\approx 10^7 \text{ mol}^{-1}\text{L s}^{-1}$ [27]. These surprisingly low values have been rationalized by some ill-defined steric effects arising from the polymer chain. According to our analysis of the published data, these values were miscalculated due to erroneous stationary concentrations of [TEMPO]. Figures 2 and 8 in Ref. [27] show a $\approx 0.2\%$ to 0.5% concentration of TEMPO under stationary conditions. This, in comparison with $[\text{TEMPO}]_0 \approx 0.04 \text{ mol/L}$, leads to $[\text{TEMPO}]_{st} \approx 10^{-5} \text{ mol/L}$. However, the authors of the original paper [27] used in all simulations a value $[\text{TEMPO}]_{st} = 0.002 \text{ mol/L}$ and 0.005 mol/L (e.g. Figs. 3 and 1 in Ref. [27]). It is difficult to explain the reasons for this miscalculation, but most likely the authors used the fractions of TEMPO present in the system instead of its absolute concentration. This led to an

erroneous TEMPO concentration that is 25 times too high and a k_d value that is 25 times too low. Thus, the lengthy discussion of the reason for the slow reaction with growing polystyryl radicals [27] is irrelevant and the real k_d values are not $1.5 \cdot 10^7 \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$ but rather $k_d \geq 10^8 \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$.

The values of the deactivation rate constants of polystyryl radicals with $\text{CuX}_2/2\text{BPY}$ are more difficult to estimate but they appear to be in the range of 10^7 to $10^8 \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$. These values are higher than the estimated rate constants for the inhibition of styrene polymerization with CuCl_2 in DMF solution, $k_{\text{inh}} \approx 2 \cdot 10^6 \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$ at 60°C [34]. It has been reported that CuBr_2 is a more powerful inhibitor than CuCl_2 and that the inhibition process has relatively high activation energy [35]. Thus, it is feasible that at $\geq 100^\circ\text{C}$, the values of the deactivation rate constant can approach the range of 10^7 to $10^8 \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$, especially with bipyridine rather than DMF ligation.

CONCLUSIONS

New controlled/"living" radical polymerizations are based on the dynamic exchange between growing radicals at very low stationary concentrations ($[\text{P}\cdot]_{\text{st}} \approx 10^{-8}$ to 10^{-7} mol/L) and a large excess of dormant species ($[\text{P-X}] \approx 10^{-2}$ to 10^{-1} mol/L). The transformation of dormant species to growing radicals may take place in the unimolecular or bimolecular process and the latter can be a catalyzed or the degenerate transfer process.

The equilibrium constants for TEMPO and ATRP styrene polymerizations are in the range of $K_T \approx 10^{-11} \text{ mol/L}$ and $K_A \approx 10^{-8}$ at $\approx 120^\circ\text{C}$. The equilibrium constant defines the overall rate of the reaction, the proportion of chains which are terminated irreversibly, and chains generated due to thermal self-initiation process. ATRP has an advantage over TEMPO, in that it is a catalytic process and that the proportion of growing radicals can be controlled additionally by a variation of the catalyst concentration.

The polydispersities in both systems are defined by the relative rates of the deactivation and propagation processes. The rate constants of deactivation are in the range of $k_d \approx 10^8 \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$, which is substantially higher than the erroneously [27] calculated rate constant for the reaction between TEMPO and growing polystyryl radicals.

EXPERIMENTAL

2,2,6,6-Tetramethyl-1-(1-phenylethoxy)piperidine was synthesized either from ethylbenzene, tert-butyl hydroperoxide and TEMPO as described before [28] or in 90% yield at 20°C via entrapment by TEMPO of 1-phenylethyl radical produced from 1-phenylethyl bromide and $\text{CuBr}/2\text{Bipy}$ in benzene. The adduct was purified by column chromatography and its purity as determined by NMR was $>98\%$. ATRP was carried out according to previously published procedures [1, 3]. Polymerizations were performed with freshly distilled styrene by dissolving

controlled amount of the initiating system and stopping the reaction by quenching it to low temperatures after variable times. Polymers were analyzed by SEC. Conversions were determined either gravimetrically or by GC following the amount of unreacted styrene.

Simulations were performed using a simulation package PREDICI which is based on an adaptive Rothe method [36, 37] as a new numerical strategy for time discretization. It uses a discrete Galerkin h-p method to represent chain length distribution and allows to follow concentration of all substrates, low and high molecular weight products and intermediates as well as molecular weights and the corresponding distributions of all types of macromolecules [38]. It has been previously reported that agreement between full analytical solutions and results obtained using PREDICI package was excellent [22].

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